INTRODUCTION

Most surfaces of minerals in glacial deposits originate as fracture surfaces (e.g., glacial flour, loess, glacio-fluvial, and glacio-lacustrine deposits). These blanket large parts of the Northern Hemisphere and in North America extend from the northernmost parts of Canada to Kansas. Similarly, the majority of mineral surfaces exposed in non-glacial sediments are fracture surfaces, produced by abrasion (traction and saltation transport) in streams, by oceanic currents, and by waves at beaches. The minerals industry generally crushes sulfide ores for processing so that the surfaces of all ores separated by flotation are fracture surfaces. Clearly, fracture surfaces are common and important in geological and minerals industry environments.

Properties and reactivity of fracture surfaces must be documented and understood to properly predict the environmental and industrial consequences of their exposure to the atmosphere and natural solutions. One means to investigate the reactivity of these surfaces is to first fracture them (in vacuo) then expose them to the atmosphere and aqueous solutions for various periods to determine the rates of reaction and mechanisms by which they react. To this end we report findings of Fe surface states on pyrite fracture surfaces.

Synchrotron radiation excited X-ray photoelectron spectroscopy (SXPS) of fractured pyrite surfaces has revealed the presence of two distinct surface states in the S 2p spectrum (Schaufuss et al. 1998a; Bronold et al. 1994). Schaufuss et al. (1998a) demonstrated that these low binding energy surface states are far more reactive than sulfur resident on bulk sites. Whereas sulfur surface states of pyrite fracture surface are now well characterized and their reactivity documented, there is a dearth of information about Fe surface states. A highly surface sensitive SXPS Fe 2p spectrum consequently was collected in an attempt to document surface states and to determine their spectral properties.

The conventional Fe 2p spectrum (AlKα source) of pristine pyrite fracture surfaces displays a strong near-symmetric peak at 707 eV and an unusual “wedge-shaped” tail on its high binding energy side (Fig. 1a). The origin of the tail is uncertain and may be: (1) a Doniach-Sunjic contribution as for metals (Nesbitt et al. 1994; Doniach and Sunjic 1970); (2) an energy

Synchrotron XPS evidence for Fe$^{2+}$-S and Fe$^{3+}$-S surface species on pyrite fracture-surfaces, and their 3D electronic states

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ABSTRACT

A X-ray photoelectron Fe 2p spectrum of a pristine pyrite fracture surface was collected using synchrotron radiation with the source tuned to 800 eV. Comparison of this highly surface sensitive Fe 2p spectrum with Fe 2p spectra collected by conventional means (1487 eV AlKα source) reveals that the high binding energy tail of the pyrite Fe 2p line results primarily from Fe surface state contributions. The three major contributions to the spectrum are interpreted to be: (1) Fe$^{2+}$ resident on bulk sites; (2) Fe$^{2+}$ resident on surfaces, edges and corners; (3) Fe$^{3+}$ surface states produced during fracture by an auto-redox reaction involving Fe and S. The intense main peak is ascribed to the bulk state, whereas the high binding energy tail of the spectrum is composed primarily of Fe$^{2+}$ and Fe$^{3+}$ surface state contributions.

Fe$^{2+}$ on bulk sites is octahedrally coordinated (O₆ symmetry). All valence electrons of Fe on bulk sites are paired (diamagnetic) and a singlet photopeak at 707 eV is consequently produced. Fracture produces Fe$^{2+}$ surface states with lower coordination than bulk sites. Fe$^{2+}$ located at surfaces, edges and corners experiences modified Ligand Field Stabilization Energies (LFSE) which results in stabilization of the dₓ² orbital and destabilization of the dₓᵧ orbital. Promotion of a dₓᵧ electron to the dₓ² orbital makes surface Fe$^{2+}$ surface states paramagnetic resulting in multiplet splitting of their associated photopeaks. The Fe$^{3+}$ surface state is necessarily paramagnetic and its photoemissions are consequently multiply split.

Analysis of photopeak structures and binding energy splittings of Fe$^{2+}$ and Fe$^{3+}$ surface states demonstrates that they are located at the appropriate binding energies, and span the appropriate energy range, to satisfactorily explain the high binding energy tail on of the Fe 2p spectrum.

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